

# **Electrolytes and separators for high voltage Li ion cells**

**(an investigation of sulfone-based  
electrolyte solvents)**

**C. Austen Angell**

**Department of Chemistry and Biochemistry,  
Arizona State University**

**March 11, 2011**

**Project ID: ES100**

**This presentation does not contain any proprietary,  
confidential, or otherwise restricted information**

# Overview

## Timeline:

Start: May 2010

Finish: Dec./2013

## Budget:

\$709,977

Funding received in FY 2010  
for 2010 and 2011

\$249,977

Funding for FY 2012

\$230,000

## Barriers:

- High viscosities, and melting points, of existing examples.
- Lack of information on additives and mixtures
- Safety issues: flammability
- Separation issues: containment impedance and toughness

## Partners:

- Oleg Borodin, U. Utah
- Goying Chen, LBL
- Brett Lucht, U. Rhode Island
- Jason Zhang, PNNL

**Relevance:** Once conductivity has been maximized, energy density and power output of VT power train can *only* be increased by increase of cell voltage. REQUIREMENT: high voltage stable electrolyte and solvent

## Background needed

Aliphatic sulfones, especially those with open-chain alkyls,<sup>10</sup> are recognized by organic chemists as unusual for their combination of polarity with resistance to both oxidation and reduction.<sup>11</sup> [Chemically, aliphatic cyclic sulfones are more easily reduced (ca. 100 times as fast) than open-chain sulfones.] The simplest mem-



**DMS**

Try destabilization of crystal lattice by making the molecule asymmetrical.

**but**

Dimethyl sulfone	$(\text{CH}_3)_2\text{SO}_2$	$T_m$ 109°C
Diethyl sulfone	$(\text{Et})_2\text{SO}_2$	70°C
Dipropyl sulfone	etc	

$T_m = 35^\circ\text{C}$ :  
eutectic  
with DMS  
is  $25^\circ\text{C}$

### High Anodic Stability of a New Electrolyte Solvent: Unsymmetric Noncyclic Aliphatic Sulfone

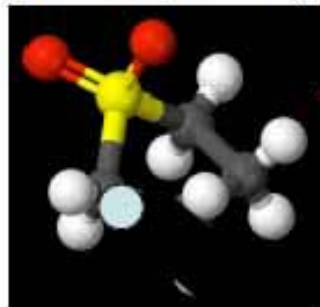
K. Xu<sup>\*,\*</sup> and C. A. Angell<sup>\*\*,\*</sup>

**5.9 V !!**

*J. Electrochem. Soc.*, Vol. 145, No. 4, April 1998

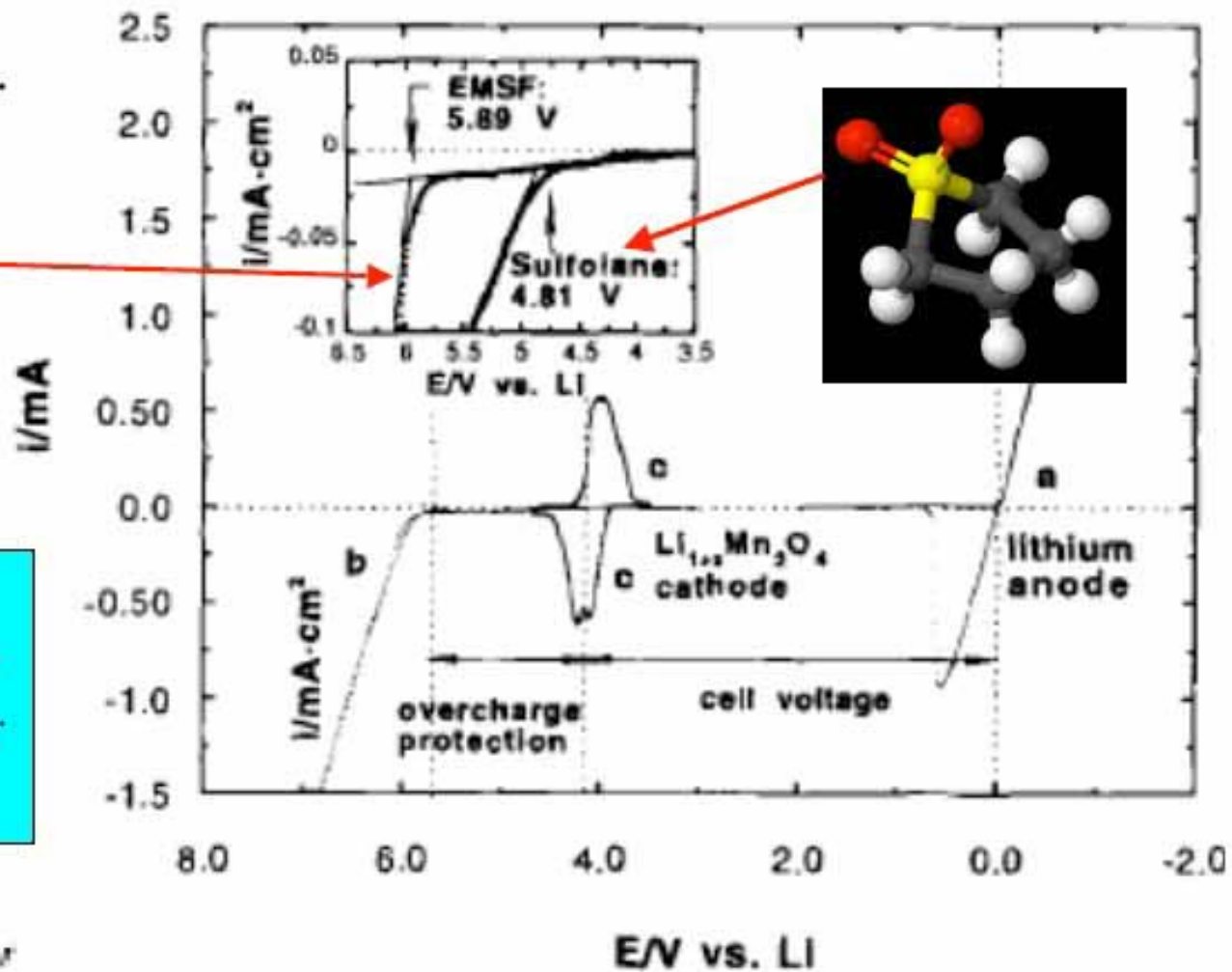
# Background: A 5.9 volt window !

Kang Xu and CAA,  
*J. Electrochem. Soc.*  
**145**, L70 (1998).



For capacitive storage, note that the energy of a capacitor is given by:

$$E = \frac{1}{8} c_p V^2 ,$$

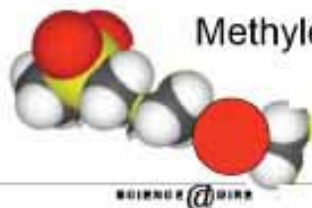




# Background: The promise of sulfones: conductivity of FEMS vs EC:DMC

US Patent No.  
6,245,465  
Angell et al., 2001

Visit by Toyota  
Delegation 2005



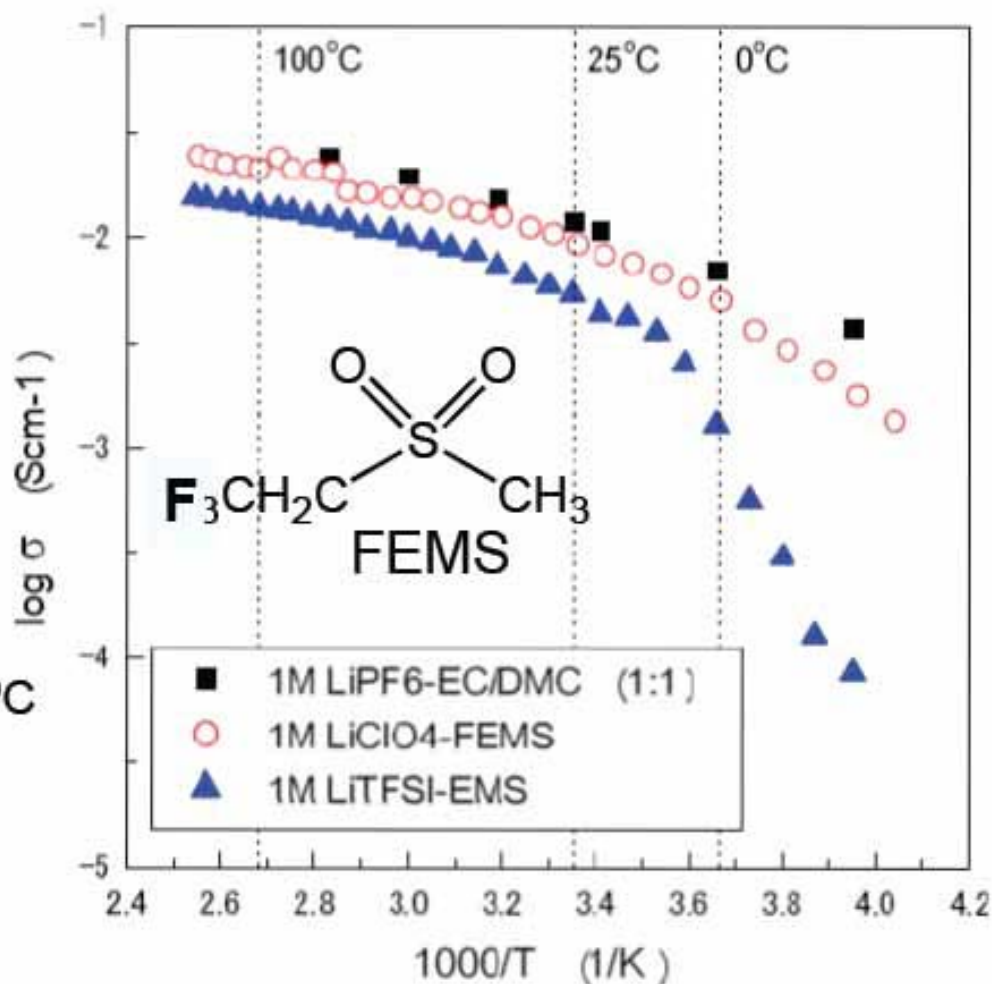
Methylethoxymethylsulfone  
(MEMS)

Melting point 7°C

Electrochemistry Communications 7 (2003) 263–266

electrochemistry  
communications  
www.electrochem.socpub.org

US Patent No. 6,245,465  
Angell & Sun., 2010  
(DOW inc option)

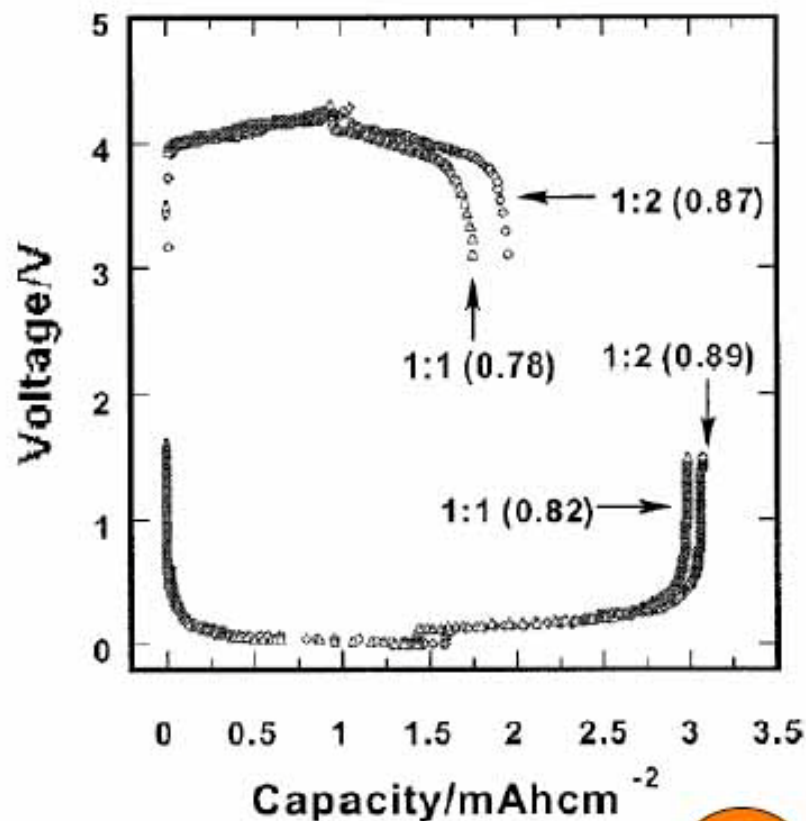
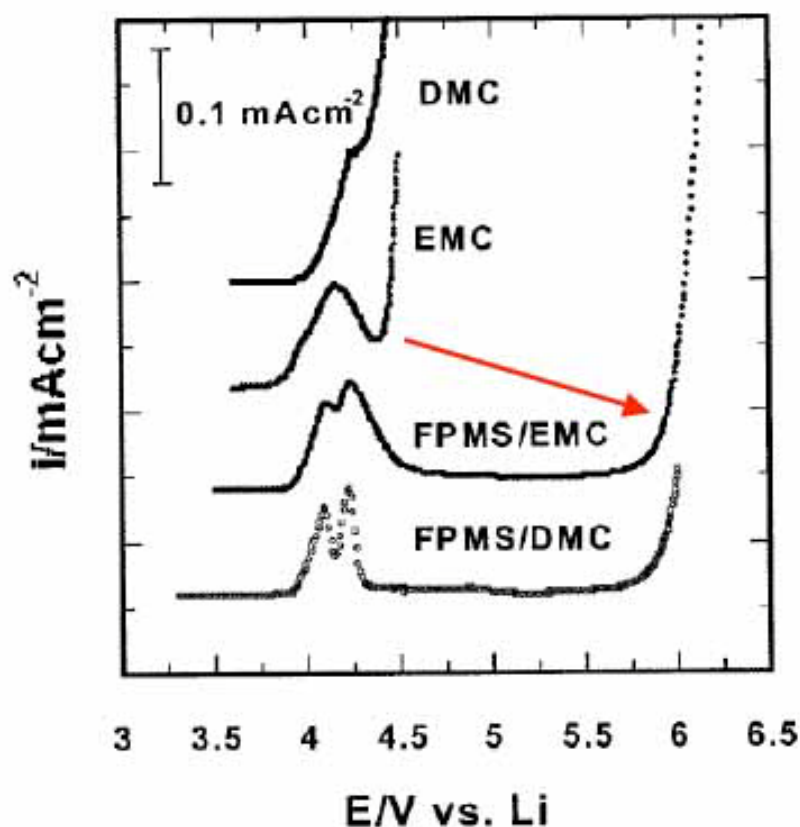


**Background:** And sulfones seem to protect lower EC “window”(but higher fluidity) co-solvents

Work of Kang Xu (JECS,2002)

**FPMS** is  $\text{CF}_3\text{CH}_2\text{CH}_2[\text{SO}_2]\text{CH}_3$

Forms good SEI



But  $T_m$  of FPMS is  $56^\circ\text{C}$

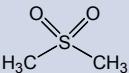
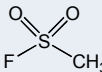
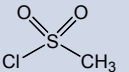
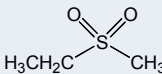
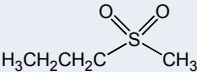
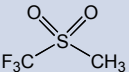
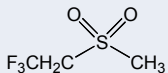
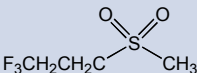
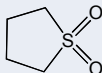
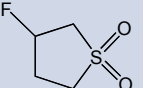


# OBJECTIVES and milestones

1. Identify unstudied sulfones for evaluation
2. Determine key properties, conductivity and “windows”, taking any commercially available cases first.
  - (a) pure sulfones (**Dec. 10, 2010**)
  - (b) mixed sulfones
  - (c) mixed sulfones and carbonates(**Dec. 10, 2010**)
3. Synthesize new sulfones
  - (a) fluorinated (**March 11, 2011**)
  - (b) fluorinated oxygenated (**March 11, 2011**)
4. Test sulfolane-based cases by synthesis, following predictions of collaborator (Oleg Borodin) (**March 11, 2011**)
5. Conceive new strategies (second year... achieved already)
6. Commence investigation of novel separator concept (**March 2011**)

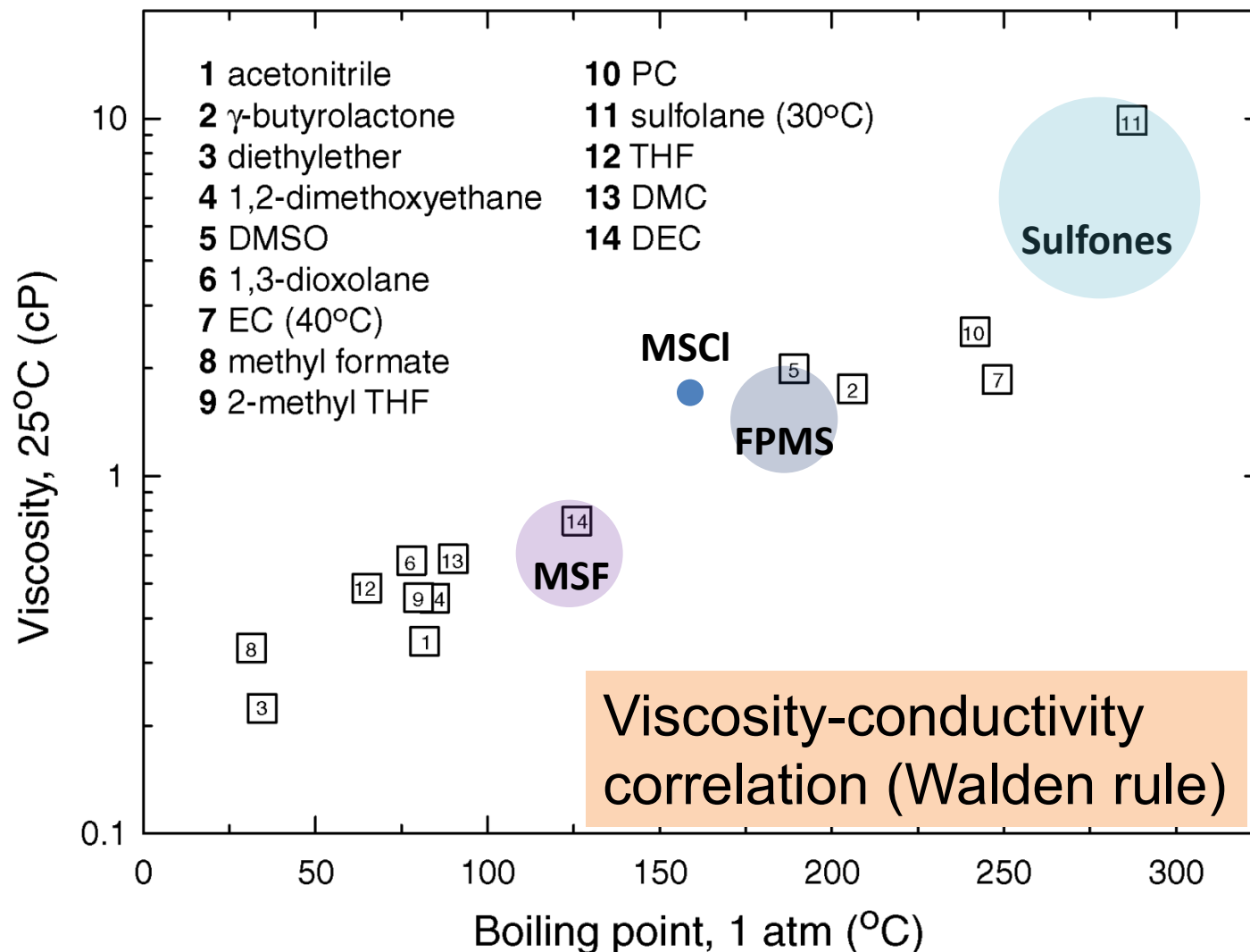


# SETTING UP: SELECTED SULFONES & THEIR PROPERTIES

	Name	$T_m$ (°C)	$T_b$ (°C)	$\eta$ (cP)	$\epsilon$	$\sigma_{25}$ (mS/cm)	Window (V vs Li/Li+)
	Dimethylsulfone (DMS)	110	(238)	-	-	-	-
	Methanesulfonyl fluoride (MSF)	-	123	-	-	3.0 (1M LiTFSI)	5.3 /LiTFSI
	Methanesulfonyl chloride (MSCl)	-33	160	1.97@25	-	-	3.7 /LiPF6
	Ethylmethylsulfone (EMS)	36.5	(240)	-	95	6.3 (1M LiTFSI) 3.2 (1M LiPF6)	5.9 /LiTFSI
	EMS-DMS eutectic (85:15 mol/mol)	25 ( $T_e$ )	-	-	-	2.2 (0.5 M LiTFSI)	-
	Methylpropylsulfone (PMS)	28	(245)	-	-	-	-
	Trifluoromethylmethylsulfone (FMMS)	-	130	-	-	-	-
	Trifluoroethylmethylsulfone (FEMS)	-	-	-	-	8.9 (1M LiClO4)	-
	Trifluoropropylmethylsulfone (FPMS)	56	180	-	-	0.035 (1M LiTFSI)	5.8 /LiPF6+DMC
	Sulfolane	27	285	10.1@30 31.2@30 (1M LiPF6)	60	3.1(1M LiTFSI) 2.5 (1M LiPF6)	5.8 /LiPF6
	3-fluorosulfolane	0.7	(303)	29.1@30 (1M LiPF6)	-	0.74 (1M LiPF6)	5.6 /LiPF6

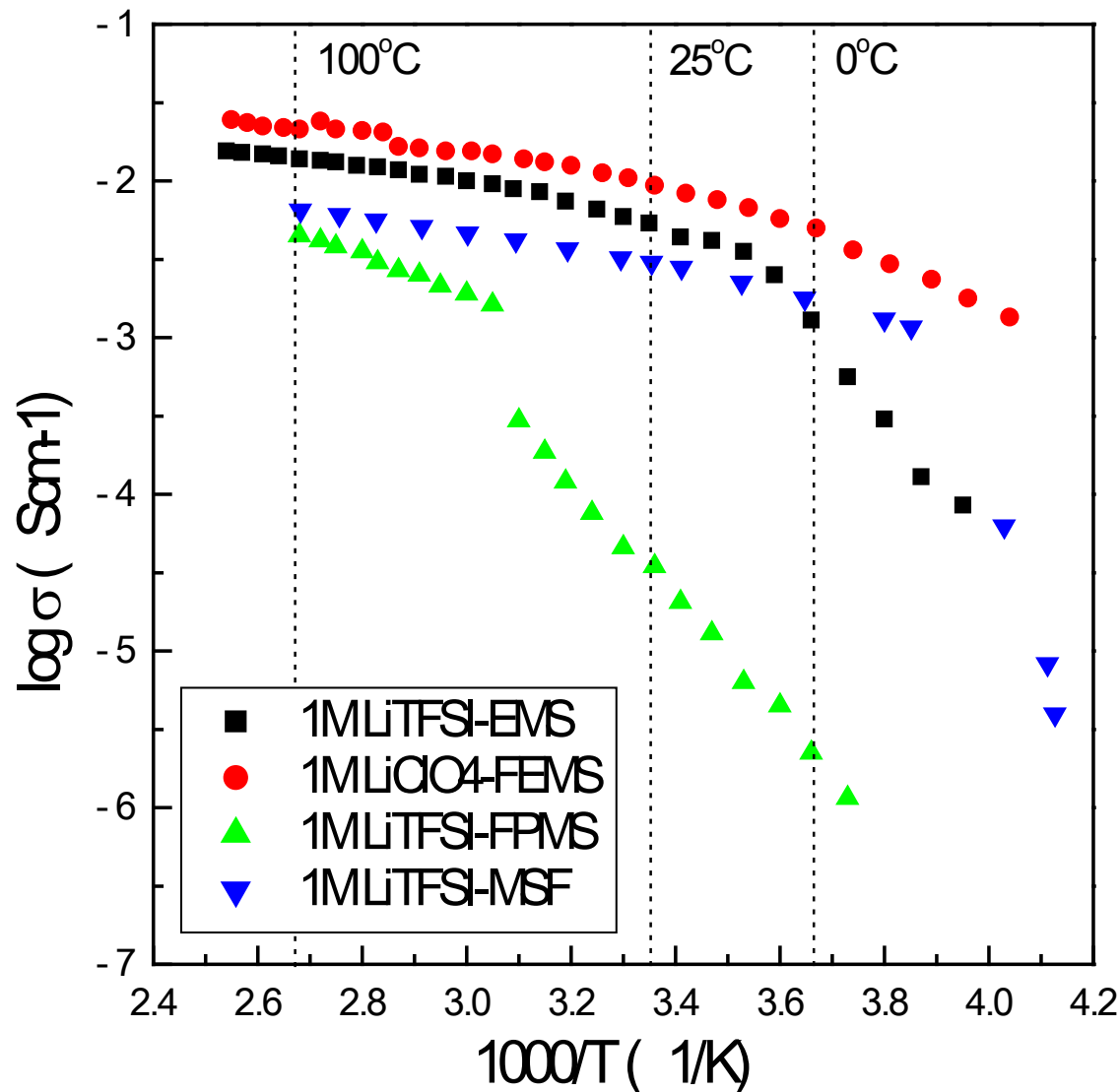


# Selection **strategies**: When no viscosity data? boiling point correlation



NEW DATA:  
Specific  
conductivities  
of various Li  
salts in sulfone  
solvents.  
The puzzle of  
low-boiling  
FPMS  
cf. MSF

## ACCOMPLISHMENTS



# The need for mixtures (see Xu review)

No single solvent can satisfy simultaneously all solvent needs

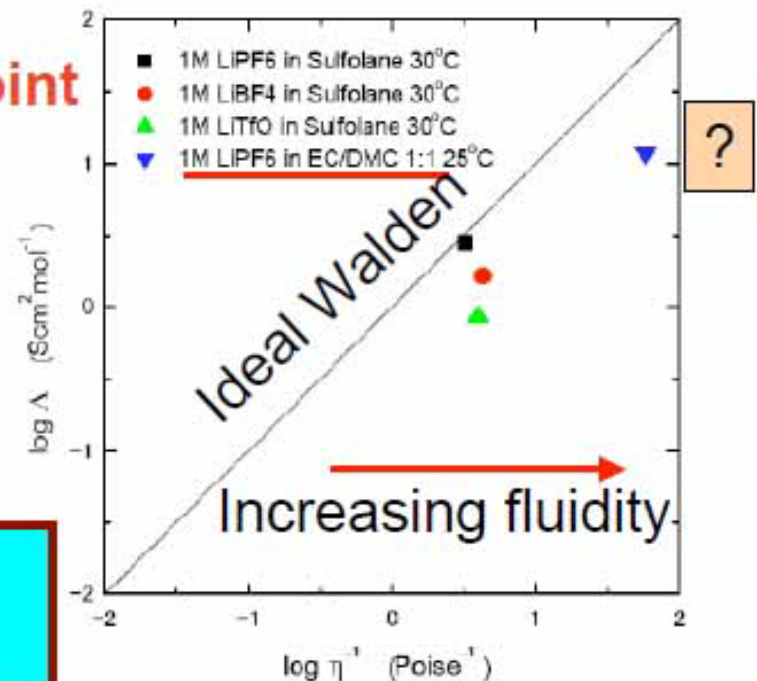
e.g Large dipole moment needed for overcoming crystal lattice energy (dissolving) causes high melting point and high viscosity, so low conductivity.

**Resolution:** mix with co-solvent of low dielectric constant and low boiling point. Thus EC-DMC

**Mixing also reduces freezing point**

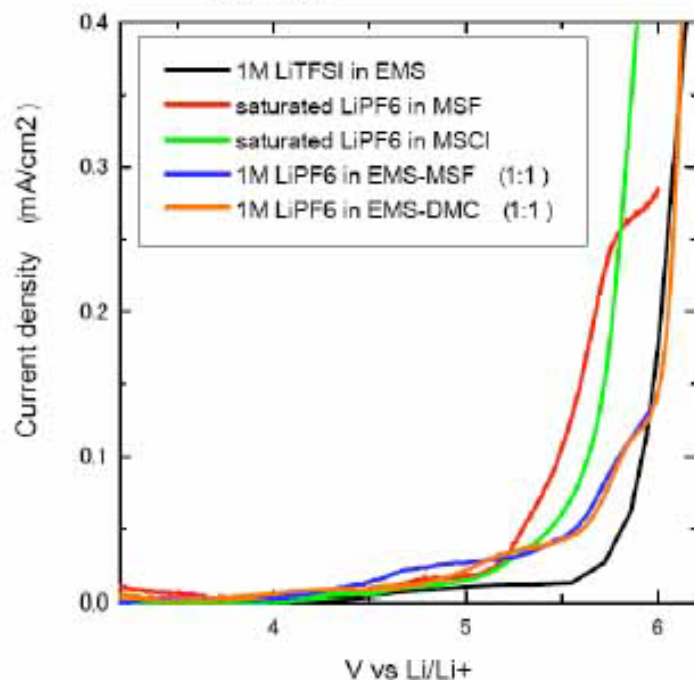
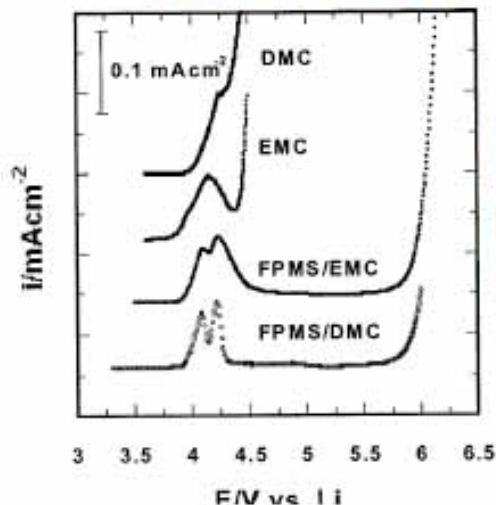
**Ionicity.** How free are the ions from one another? Are we optimizing the decrease of viscosity, or losing some of the ions to associated pairs?

The first Walden plot for Li battery electrolytes

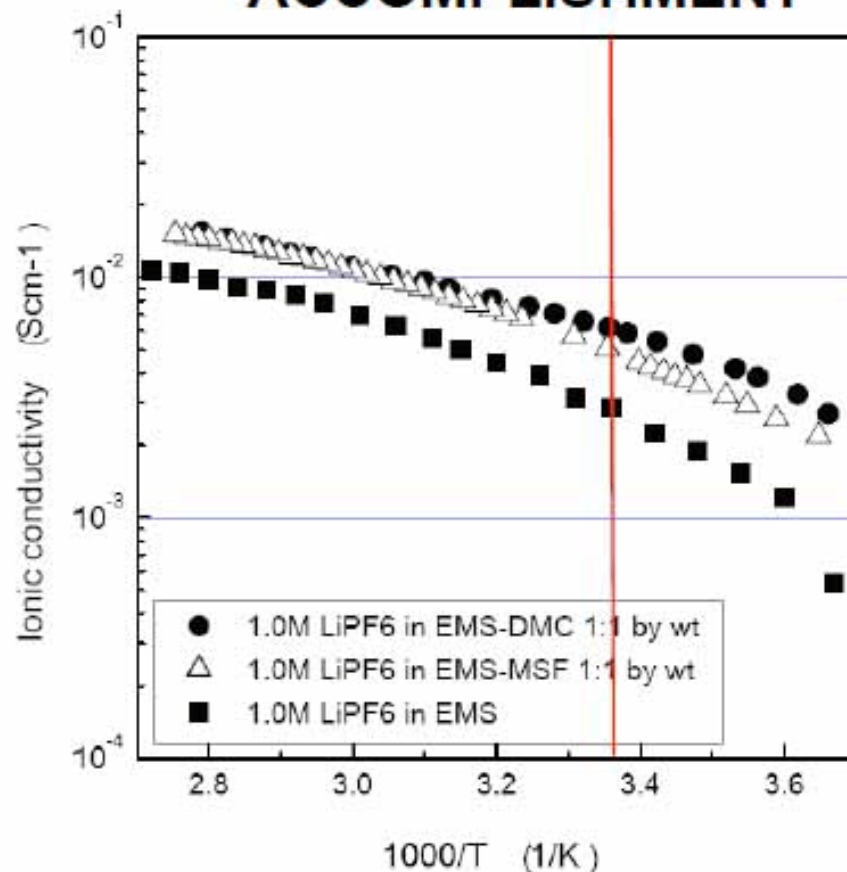


# The mixture strategy: EMS vs new mixtures.

Earlier work from Kang Xu & CAA (JECS 2002) suggested mixture synergism



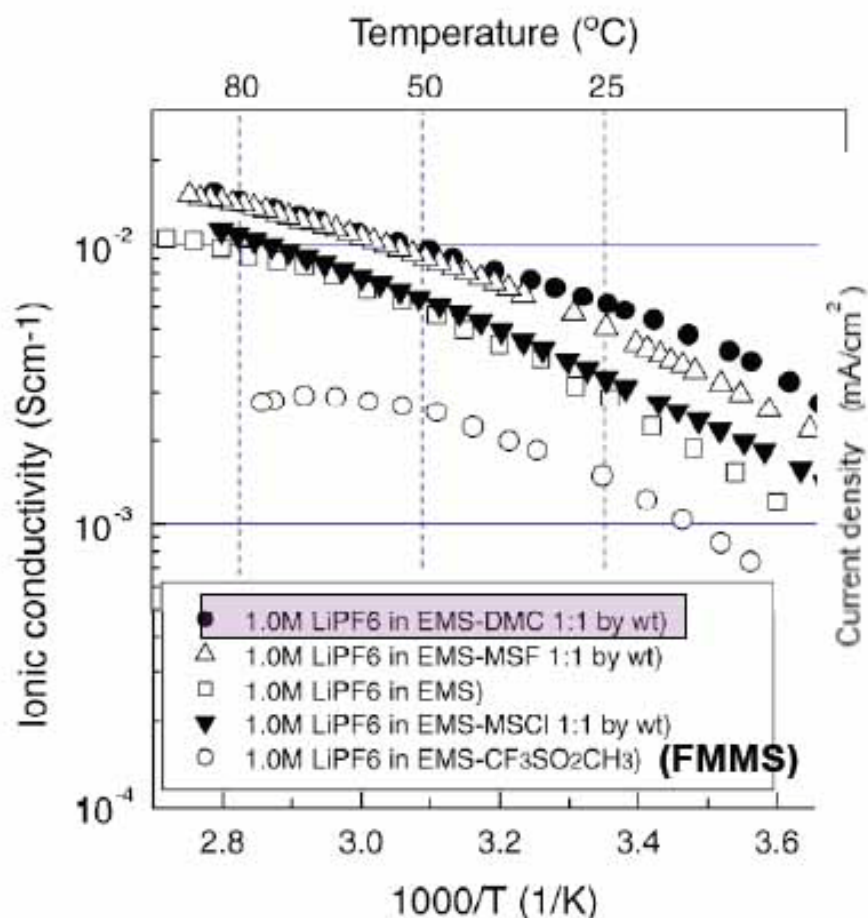
## ACCOMPLISHMENT



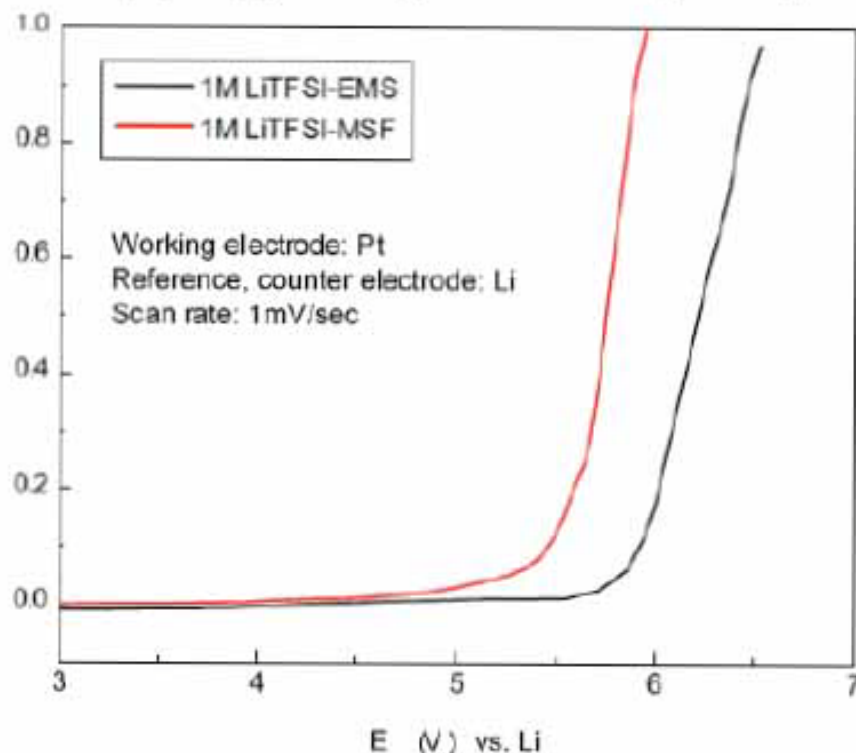


# Other interesting mixtures (with high fluidity MSF)

## Accomplishment slide

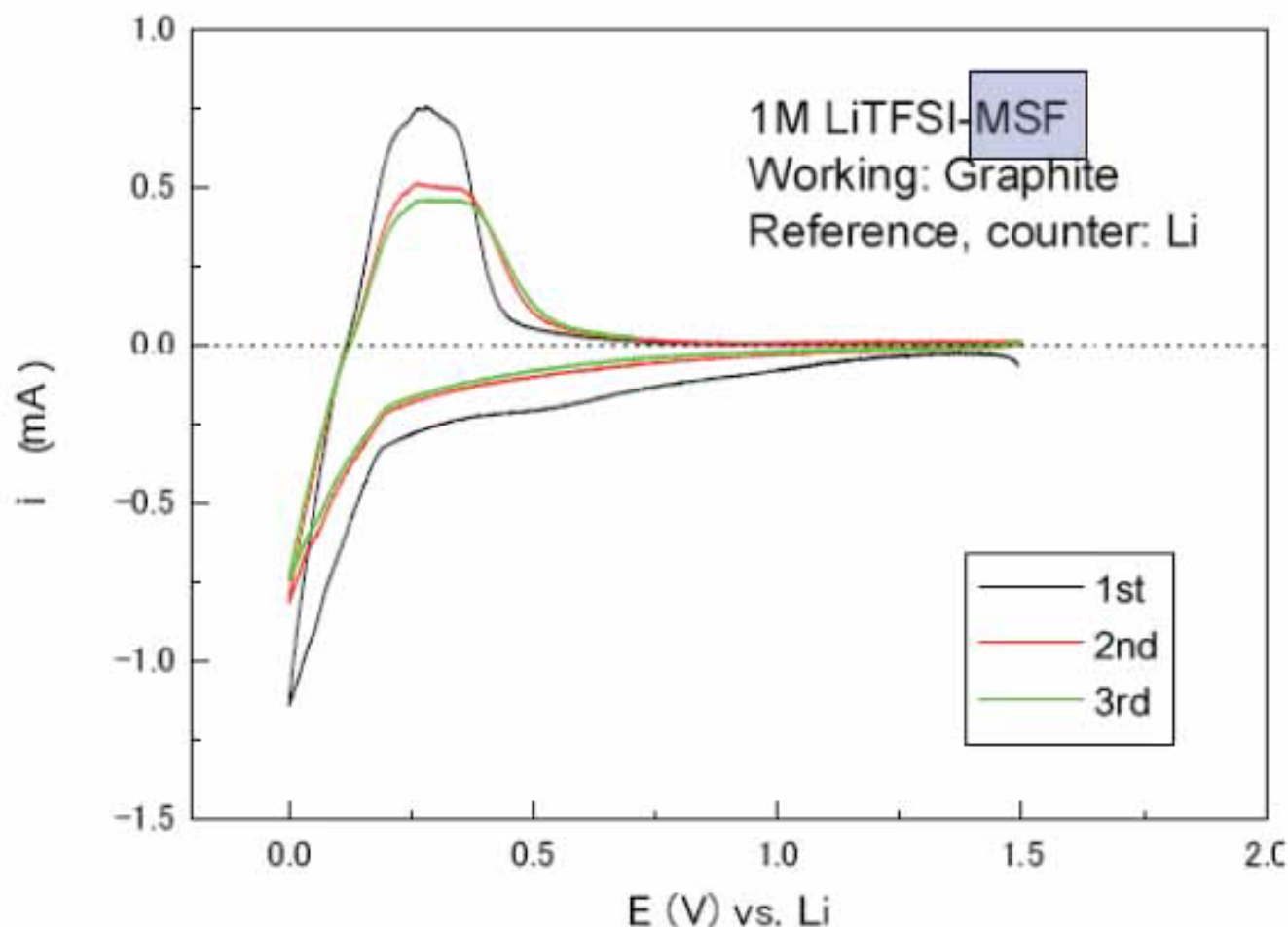


EMS-MSF not only has good conductivity and window, but also good Li deposition and stripping, i.e. good SEI (next)



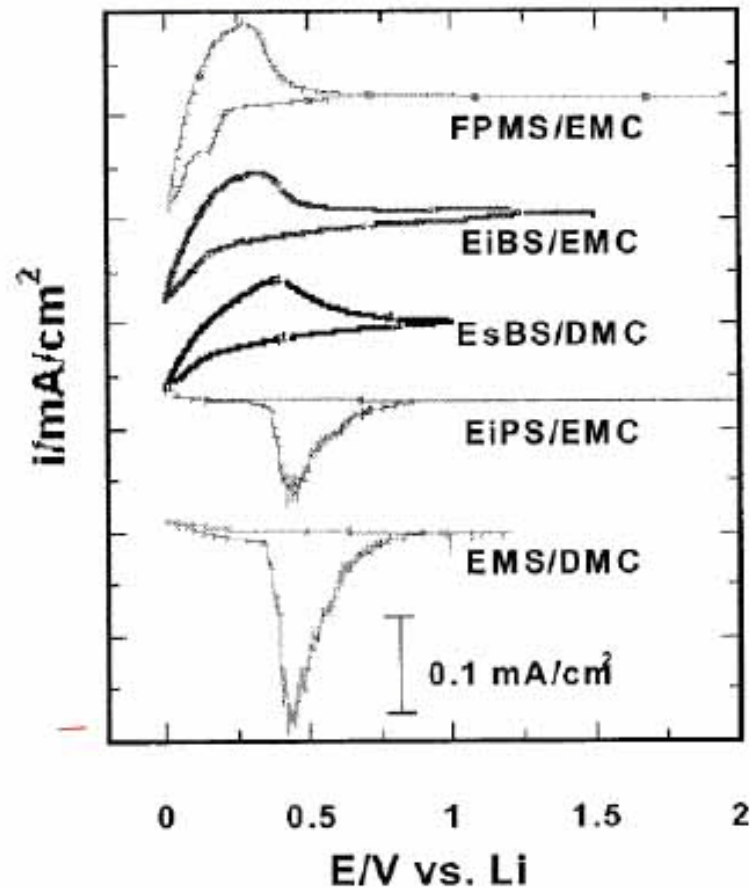
## ACCOMPLISHMENT SLIDE

# Lithium deposition and stripping in MSF & EMS-MSF solutions

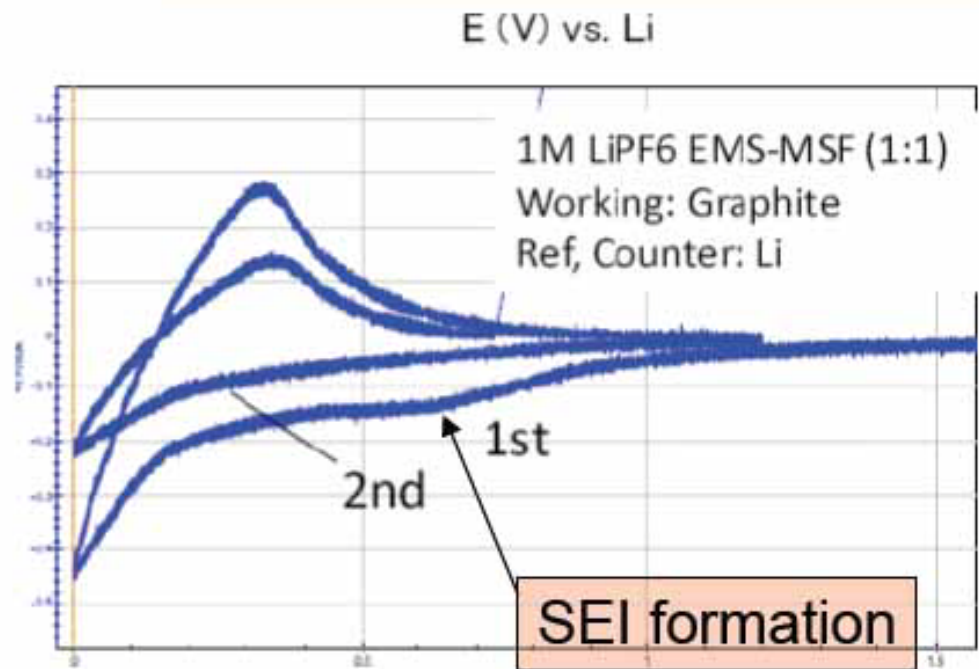


# Lithium deposition and stripping in MSF & EMS-MSF solutions

From Xu and Angell  
JECS (2001)

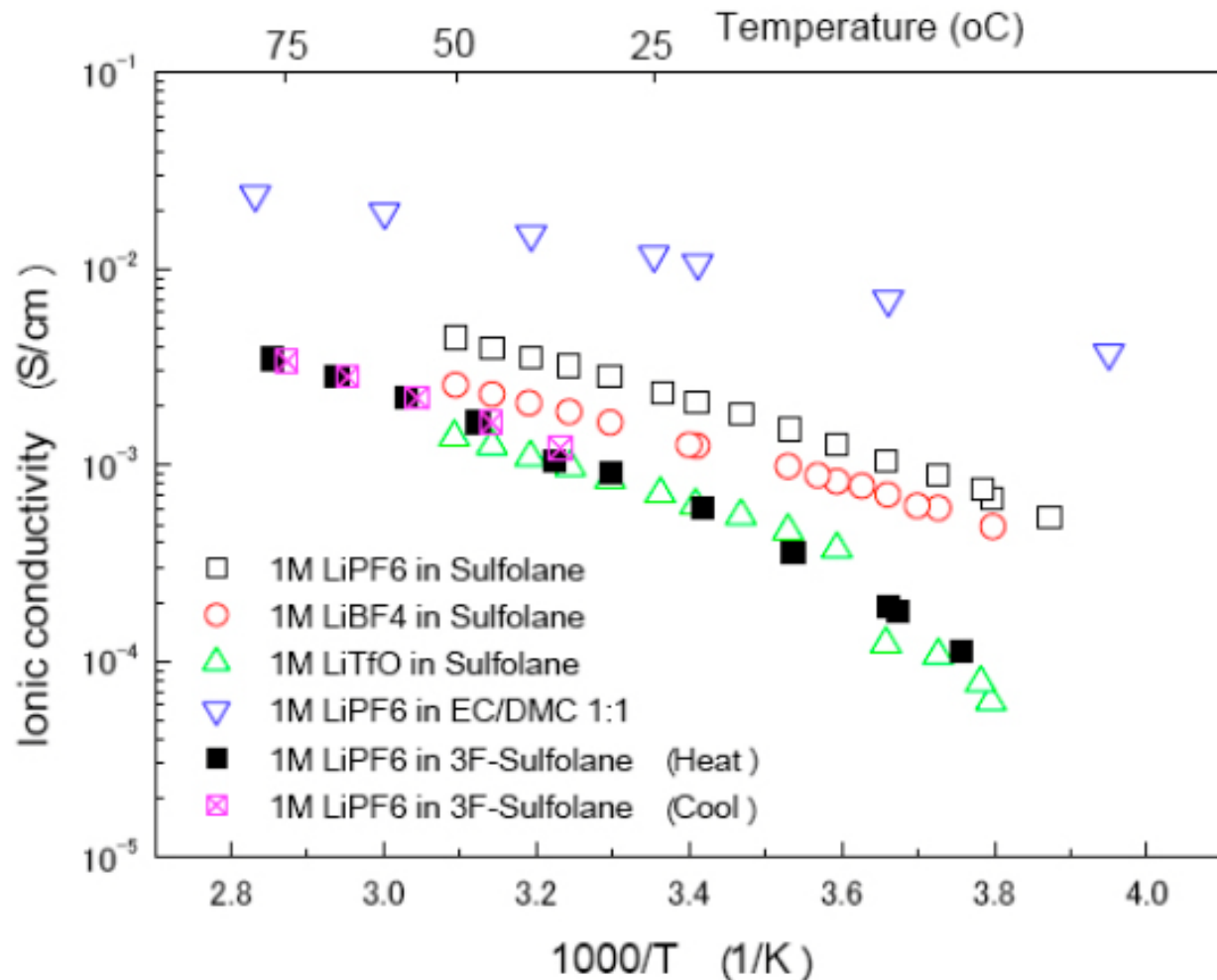


**Accomplishment slide:**  
formation of effective SEI in  
EMS-MSF solution



## ACCOMPLISHMENT SLIDE

Conductivity Arrhenius plots for sulfolanes and fluorinated sulfolane, relative to EC:DMC.  
Can we improve on things with fluorination?



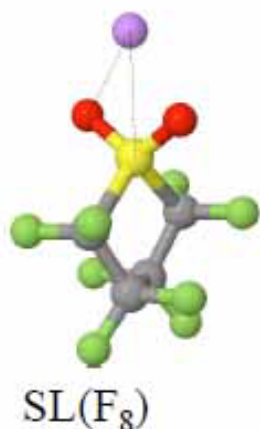
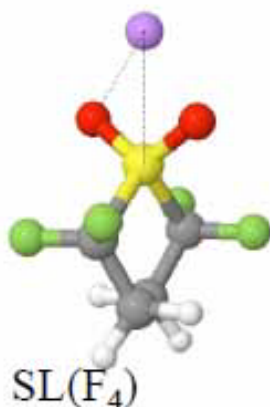
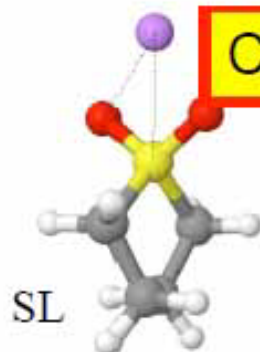
Fluorination  
can improve  
fire resistance



## Contribution from Collaborating laboratory- **Oleg Borodin**

### Fluorinated Solvents

- ★ Influence of sulfolane fluorination on the solvent oxidative stability, transport properties and its ability to coordinate  $\text{Li}^+$  has been investigated complementing experimental studies that are currently performed by Austen Angell group (ASU)



The  $\text{Li}^+$ /solvent binding energy (in kcal/mol) from QC

	$\text{Li}^+/\text{SL}$	$\text{Li}^+/\text{SL}(\text{F}_4)$	$\text{Li}^+/\text{SL}(\text{F}_8)$	$\text{Li}^+/\text{EC}$	$\text{Li}^+/\text{DMC}$
MP2/cc-pvTz or <i>MP2/aug-cc-pvTz</i>	-52.7	-40.8	-29.5	<b>-47.5</b>	<b>-40.9</b>
Solvent self-diffusion coefficient					
T (K)	303	303	303	313	298
D ( $10^{-10} \text{ m}^2/\text{s}$ )	1.1	2.5	4.7	8	25.4

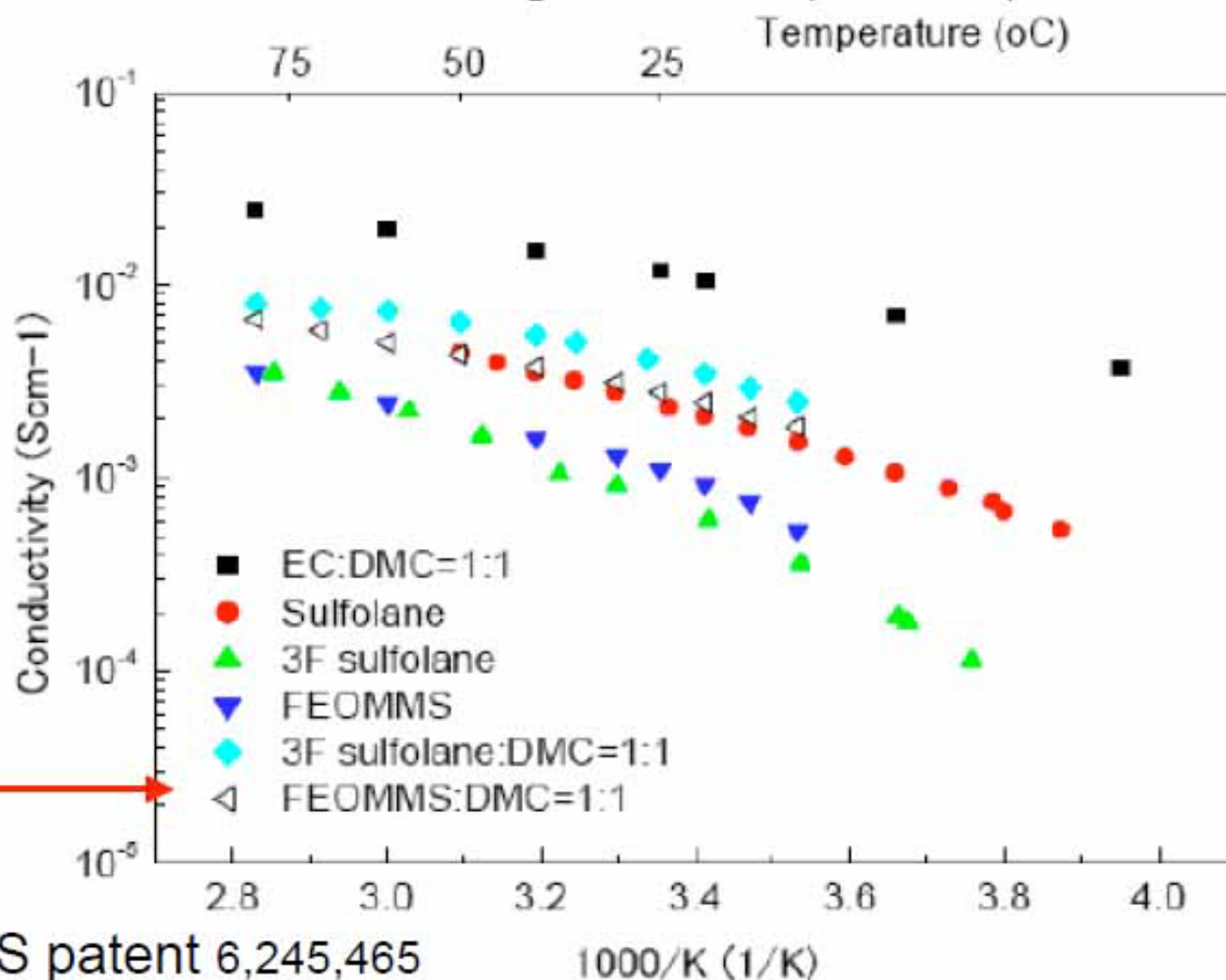
- ★ Completely fluorinated  $\text{SL}(\text{F}_8)$  is not expected to be good solvent for typical Li salts such as  $\text{LiPF}_6$  or  $\text{LiTFSI}$ .
- ★ Semifluorinated sulfolane  $\text{SL}(\text{F}_4)$  is expected to have lithium salt dissociation similar to DMC, while  $\text{SL}(\text{F}_4)$  dynamics is predicted to be a factor of 2.5 faster than SL but a factor of five slower than DMC.

**OTHER COLLABORATIONS:** The order-disorder transition in  $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$  (with **Guoying Chen**, LBL)

## ACCOMPLISHMENT/COLLABORATION SLIDE

# Sulfolane-based systems

With collaboration of Oleg Borodin (U. Utah)



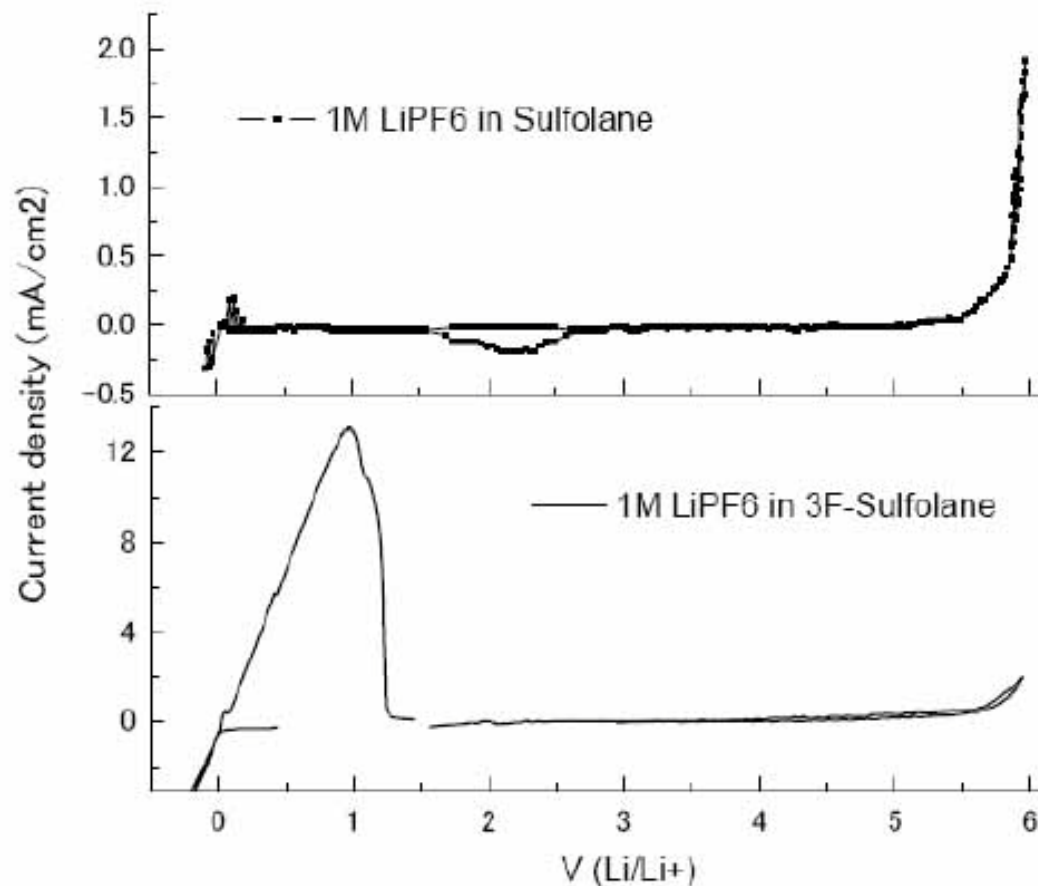
And a  
fluorinated  
ethersulfone

Follow-up of US patent 6,245,465

## ACCOMPLISHMENT SLIDE

### Good electrochemical aspects of fluorinated sulfolane

- Complete deposition and subsequent stripping of Li in fluorinated sulfone. No extraneous processes.
- Excellent wide electrochemical window





# NEXT: Keeping the electrolyte in place

## The separator problem

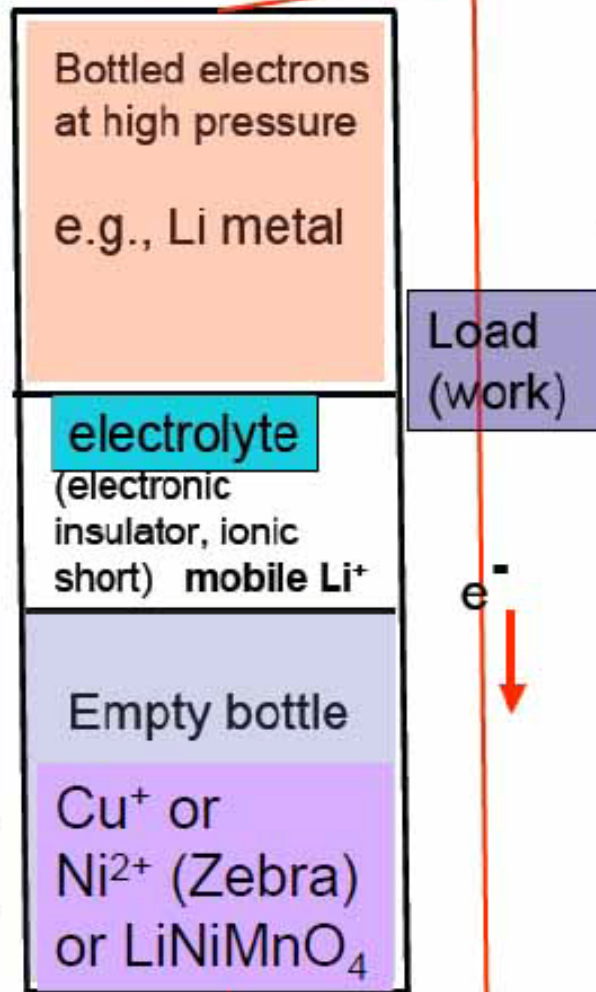
Electrolyte is mobile liquid: It can be kept in the right place by

1. soaking it up in some sort of sponge:porous medium with wettable surfaces,
2. or creating a solid around it by using a polymerizing component which is then reacted.

### EXAMPLES

1. Celgard is a microporous polypropylene membrane surface-derivatized to soak up carbonate solvents.
2. **methacrylate** can be added to the electrolyte and then thermally, or by light, polymerized to create a gel (costs conductivity)

NOW: a novel solution - nanoporous membrane strategy: the Maxwell slat net by rigidity percolation.





# **TECHNICAL BACKUP SLIDES**



# From K. Xu, Chem. Reviews

*Chem. Rev.* **2004**, *104*, 4303–4417

## Organic Carbonates and Esters as Electrolyte Solvents

Solvent	Structure	M. Wt	T <sub>m</sub> / °C	T <sub>b</sub> / °C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T <sub>f</sub> / °C	d/gcm <sup>-3</sup> , 25 °C
<b>EC</b>		88	36.4	248	1.90, (40 °C)	89.78	4.61	160	1.321
<b>PC</b>		102	-48.8	242	2.53	64.92	4.81	132	1.200
<b>BC</b>		116	-53	240	3.2	53			
<b>γBL</b>		86	-43.5	204	1.73	39	4.23	97	1.199
<b>γVL</b>		100	-31	208	2.0	34	4.29	81	1.057
<b>NMO</b>		101	15	270	2.5	78	4.52	110	1.17
<b>DMC</b>		90	4.6	91	0.59 (20 °C)	3.107	0.76	18	1.063
<b>DEC</b>		118	-74.3 <sup>a</sup>	126	0.75	2.805	0.96	31	0.969
<b>EMC</b>		104	-53	110	0.65	2.958	0.89		1.006
<b>EA</b>		88	-84	77	0.45	6.02		-3	0.902
<b>MB</b>		102	-84	102	0.6			11	0.898
<b>EB</b>		116	-93	120	0.71			19	0.878

# Issues with liquid electrolytes

1. Ionic shorts.... Wot to do?
2. With in situ polymerization to yield gel, the conductivity decrease always seems to be larger than tortuosity constants would e expected to account for.
3. Conductivity reduction: with celgard the reduction in conductivity should just decrease by a tortuosity factor
4. A new idea, the variable nanoporous net the Maxwell rigidity, and the Phillips-Thorpe rigidity percolation model